REMARKS

Claims 9-37 are currently pending in the instant application.

The Specification has been amended to delete the original section headings and to insert the preferred section headings pursuant to 37 C.F.R. §1.77. A new Title of the Invention has been inserted. An Abstract of the Disclosure, in accordance with the disclosure, has been added. It is submitted that the amendments to the Specification made herein introduce no new matter. All of the amendments to the Specification constitute deletions of original section headings and/or paragraphs, and insertions or additions of new section headings and/or paragraphs. Accordingly, pursuant to 37 C.F.R. §1.121(b)(1)(iii), no separate page captioned "VERSION WITH MARKINGS TO SHOW CHANGES MADE" is necessary. A separate page containing a clean copy of the Abstract of the Disclosure has been attached for the Examiner's convenience. Entry of the amendments to the Specification made herein are therefore proper and respectfully requested.

Original claims 1-8 have been canceled and replaced with new claims 9-37 solely for the purpose of improving clarity and grammar, which may suffer in translation, and not for any reason which relates to the statutory requirements for a patent. New claims 9-37 have not been added in response to any rejection, nor in anticipation of any rejection. Applicants respectfully submit that the scope of new claims 9-37 generally corresponds to the scope of original claims 1-8, and that new claims 9-37 are no narrower than original claims 1-8. Furthermore, although a moot point in view of their cancellation, Applicants respectfully submit that original claims 1-8 satisfied the requirements of 35 U.S.C. §112, as filed. New claims 9-37 are supported by the claims as originally filed and in the Specification, for example, at page 2, lines 14-30; at page 3, lines 5-9 & 14-30; and in the Examples. No new matter has been introduced. All of the amendments to the Claims constitute cancellation of original claims and the addition of new claims. Accordingly, pursuant to 37 C.F.R. §1.121(c)(1)(ii), no separate page captioned "VERSION WITH MARKINGS TO SHOW CHANGES MADE" is necessary. Entry is therefore proper and respectfully requested.

Preliminary Amendment of U.S. National Stage for International Application PCT/EP00/00903 filed February 4, 2000

Prompt examination of the instant application in view of the amendments made herein is respectfully requested.

Respectfully submitted,

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August 13, 2001
(Date)

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518 Rec'd PCT/PTO 13 AUG 2001

Method for Producing Phytosterols

Field of the Invention

This invention relates generally to food additives and more particularly to a new process for the production of phytosterols substantially free from citrostadienol.

Prior Art

Phytosterols and their esters possess hypocholesterolaemic properties, i.e. these substances are capable of lowering the cholesterol level in the blood. Accordingly, they are used as food additives, for example for the production of margarine, frying oils, sausage, ice cream and the like. The production of sterols and other unsaponifiable constituents, such as tocopherols for example, from distillates obtained in the deacidification of vegetable oils, has already been variously described in the literature, cf. **EP-A2 0 610 742** (Hoffmann-LaRoche), **GB-A1 2,145,079** (Nisshin Oil Mills Japan) and **EP-A1 0 333 472** (Palm Oil Research and Development Board).

European Patent **EP-B1 0 656 894** (Henkel) describes a process for the production of sterols in which a residue from the distillation of methyl esters consisting essentially of glycerides, sterols, sterol esters and tocopherols is transesterified with methanol in the presence of alkaline catalysts. After neutralization of the catalyst, removal of the excess methanol by distillation and, optionally, removal of the catalyst by washing, the sterols are crystallized by lowering the reaction temperature from about 65 to 20°C. The crystals obtained are then washed with methanol and water. However, where residues from the production of methyl esters based on sunflower oil are used, the sterols obtained contain not only the

target components, such as above all campesterol, campestanol, stigmasterol, β-sitosterol and β-sitostanol, but also significant amounts of citrostadienol which is undesirable for applicational reasons. German patent application **DE-A1 3226225** (Raisio) describes a process by which the amount of citrostadienol can be reduced. In this process, the solid sterols are first dissolved in heptane and then re-crystallized after addition of methanol. However, the resulting products are by no means free from citrostadienol and, in addition, the yields are unsatisfactory.

Accordingly, the problem addressed by the present invention was to provide high yields of phytosterols which would be distinguished above all by the fact that they would be largely free from citrostadienol.

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Description of the Invention

The present invention relates to a process for the production of phytosterols by alkali-catalyzed transesterification of residues from the production of methyl esters with methanol, neutralization of the catalyst and removal of the unreacted alcohol, characterized in that the transesterification products are dissolved in saturated hydrocarbons containing 5 to 10 carbon atoms at a temperature at which they are present in liquid form, the phytosterols are crystallized in the hydrocarbon by lowering the temperature, optionally after the addition of an adequate quantity of aqueous methanol, and are then removed and purified in known manner by filtration, washing and drying.

It has surprisingly been found that crystallization of the sterols in hydrocarbons coupled with the addition of effective quantities of aqueous methanol gives products which have citrostadienol contents below 0.5% by weight and preferably below 0.2% by weight and which are therefore substantially free from this unwanted component. Another advantage is that, in contrast to known processes, the yields of sterol in the crystallization step are significantly higher.

Detailed Description of the Invention

Transesterification

The production of a sterol-rich fraction by transesterification of residues from the deacidification of vegetable oils and subsequent working up can be carried out as described in EP-B1 0 656 894. Suitable starting materials are the distillation residues obtained, for example, as so-called deodorizer condensates in the production of fatty acid methyl esters based on rapeseed oil or, more particularly, sunflower oil. Tall oil pitch, more particularly pitch obtained from birch bark, is also suitable. Where it relates to the production of the sterol fractions, reference is comprehensively made to the document cited above.

Crystallization

A key feature of the new process is that the products obtainable from the transesterification are dissolved in the hydrocarbons at a temperature at which they are still liquid. This is preferably the case at 60 to 80°C and more particularly at 65 to 70°C. Suitable solvents are lower alkanes, for example pentane, hexane, heptane, octane, nonane and decane. Included herein are both the linear hydrocarbons and the branched structural isomers derived therefrom and mixtures thereof. However, the use of hexane, heptane or mixtures thereof has proved to be particularly advantageous. After the sterols have dissolved, the temperature is reduced to such a value that the pure sterols crystallize. It has proved to be of advantage in this regard to add an effective quantity of aqueous methanol to the mixture. 1 to 25% by weight aqueous methanol solutions are normally used for this purpose, the quantity in which they are added - based on the hydrocarbons - typically being in the range from about 1 to 15% by weight. Although the crystallization process begins at a temperature as low as about 30°C, it has proved to be of advantage to lower the temperature to about 15 to 25°C. The phytosterols obtained are

then removed and purified in known manner, i.e. filtered off, washed free from soaps and then dried to constant weight. The resulting products have a citrostadienol content of less than 0.5% by weight and preferably less than 0.2% by weight.

Examples

Example 1. 200 g of a distillation residue from the production of sunflower oil fatty acid methyl ester containing inter alia 15% by weight of glycerides and 28% by weight of free or bound sterols were introduced together with 78 g of methanol into a 1-liter three-necked condenser equipped with a stirrer and distillation head. 3.8 g of 30% by weight sodium methylate solution were then added to the mixture, followed by stirring for 4 h at 70°C. The alkaline catalyst was then neutralized by addition of 4.2 g of citric acid dissolved in 19 g of methanol, the unreacted methanol was distilled off in vacuo and the residue was washed soap-free with water at 65°C. A mixture of 400 g of hexane, 26 g of methanol and 8 g of water was added to the crude product and the whole was cooled to 20°C. Removal of the mother liquor through a filter and drying of the residue left 41 g of sterols which were free from citrostadienol.

Example 2. The procedure was as described in Example 1 except that a mixture of 200 g of heptane, 13 g of methanol and 4 g of water was added to 100 g of the transesterification product and the whole was cooled for 4 hours to 20°C. Filtration and drying left 19.4 g of sterols with a citrostadienol content of less than 0.2% by weight.

Comparison Example C1. The procedure was as described in Example 1 except that methanol was added to the transesterification product in a ratio by weight of 1:1. On cooling to 20°C, the crystals precipitated and were

filtered off, washed with aqueous methanol and then dried. However, the resulting sterols still contained 4.7% by weight of citrostadienol. 100 g of this product were dissolved in heptane at 70°C and, after the addition of 20 g of methanol, the whole was again cooled for 4 hours to a temperature of 20°C. Filtration and drying left only 75 g of sterols still with a citrostadienol content of 4.2% by weight.

CLAIMS what is claimed is?

1. A process for the production of phytosterols by alkali-catalyzed transesterification of residues from the production of methyl esters with methanol, neutralization of the catalyst and removal of the unreacted alcohol, characterized in that the transesterification products are dissolved in saturated hydrocarbons containing 5 to 10 carbon atoms at a temperature at which they are present in liquid form, the phytosterols are crystallized in the hydrocarbon by lowering the temperature and are then removed and purified in known manner by filtration, washing and drying.

2. A process as claimed in claim 1, characterized in that residues from the production of sunflower oil fatty acid methyl esters or tall oil pitch are used.

3. A process as claimed in claims 1 and/or 2, characterized in that the transesterification products are dissolved at 60 to 80°C.

4. A process as claimed in at least one of claims 1 to 3, characterized in that hexane, heptane or mixtures thereof is/are used as the solvent.

5. A process as claimed in at least one of claims 1 to 4, characterized in that an effective quantity of aqueous methanol is added during crystallization.

6. A process as claimed in at least one of claims 1 to 5, characterized in that 1 to 25% by weight aqueous methanol solutions are used.

7. A process as claimed in at least one of claims 1 to 6, characterized in that the aqueous methanol solutions are used in quantities of 1 to 15% by weight, based on the hydrocarbons.

8. A process as claimed in at least one of claims 1 to 7, characterized in that phytosterols with a citrostadienol content of less than 0.5% by weight are produced.

Ersatzblatt (Regel 26)